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Intermediate technologies towards low-carbon economy. The Greek zeolite CCS outlook into the EU commitments

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ABSTRACT

Technological premises for a successful economical path toward low carbon economy are described. It is attempted to relate fossil fuels (lignite) combustion with the requirements for sustainable energy production in Greece proposing economic, feasible and environmentally friendly methods for minimization of the CO_2 problem using innovative techniques for separation, carbon capture and storage (CCS) of this greenhouse gas. CCS constitutes an intermediate perspective to a low carbon energy production. Inexpensive and efficient methods of CCS can be achieved by new physicochemical methodologies enhancing the adsorption driven carbon dioxide capture in zeolite voids or in depleted lignite matrices, eventually by exploitation existing natural Greek deposits. The large scale application of a recently developed method leading to a high CO_2-over-N_2 selectivity and adsorption capacity NaKA Zeolite is examined.
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Contents

Abbreviations: APTES, amino-propyl-tri-ethoxy-silane; CCS, carbon capture and storage; EEA, European environmental agency; EOR, enhanced oil recovery; ESA, electrical swing adsorption; ETS, emission trading system; EU-27, European Union of 27 members; FTIR, Fourier transform infrared spectrometer; GDP, gross domestic product; GHG, greenhouse gases; kt CO_2-eq, kilo tones carbon dioxide equivalents; LFFE, low fossil fuel economy; LCE, low-carbon economy; LTA, Linde Type A zeolite structure; TPES, total primary energy supply; PSA/VPSA, pressure/vacuum swing adsorption; RES, renewable energy sources; SEM, scanning electron microscope; TSA, temperature swing adsorption; UNCED, United Nations Conference on Environment and Development; XRD, X-ray diffraction.

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1. Introduction

For more than two centuries, coal has been a significant source of energy for developing and industrial countries. Already for several decades ago coal production as energy source, however, has been connected with environmental problems and human health costs [1]. Because anthropogenic emissions of carbon dioxide result primarily from the combustion of fossil fuels, world energy use continues to be at the center of the climate change debate. Coal provides the fuel for 39% of electricity production globally, and will continue to make an important contribution to energy security because of its widespread geographic distribution, and the extent of available resources relative to anticipated energy needs [2].

The United Nations Conference on Environment and Development (UNCED) [3] and the successive protocol adopted on December 11, 1997 in Kyoto, Japan aimed at fighting global warming and committed themselves to a reduction of greenhouse gases (GHG). The European Union is committed under the Kyoto Protocol, to reduce GHG emissions by 8% from 1990 levels by 2008–2012. According to EU the total compliance costs of meeting the Kyoto Protocol targets could be as low as 0.06% of EU produced GDP in 2010, if the EU should adopt the most efficient policies to reduce GHG emissions. The Protocol sets obligatory targets for 37 industrialized countries and the EU for reducing GHGs [4].

During the past years in the EU and the other Kyoto participating countries, it has become an important priority as response to the global warming problem [5], to promote, a low-carbon economy (LCE). As the effects of climate change become more evident, cutting carbon emissions has to become a focal point for all types of initiatives [6], including extensive GHG emissions from large-scale industrial meat production [7]. The LCE or low fossil fuel economy (LFFE) is an economy, which has a minimal output of GHG emissions into the atmosphere and particularly refers to the greenhouse gas, carbon dioxide, CO_2. This economy is characterized by low energy consumption, low material consumption, low emission and low pollution and should be one of the present choices in the EU adopted framework of sustainable development.

In order to fulfill the Kyoto protocol, Greece initiated its National Program for Climate Change and has already adopted measures including participation of an EU-wide emissions trading system, a strategy to increase the use of alternative road fuels and improvements in the energy efficiency of buildings [8]. In addition, measures have been taken on energy efficiency, promotion of combined heat and power, shifting the balance towards less polluting modes of transport and restrictions of using fluorinated gases.

The development of the low carbon economy is based on the concern of the international community for the harmful result from the emission of greenhouse gases, CO_2 in particular. However, the impact of the new, low carbon economy on the traditional industry, which is based on fossil fuel resources has to be also studied and some alternative methods to develop low-carbon economy have to be proposed. Carbon capture and storage is considered as one of the most promising technological options for the limitation of CO_2 emissions from the power generation sector and other carbon-intensive industries [9]. The conventional process for carbon dioxide capture is by use of reversible solvent absorption [10]. In general, this process involves high energy consumption since, e.g. regenerating the solvent requires a high heating utility. The associated cost and environmental impact implies the need for other more efficient separation processes to be applied to carbon dioxide capture [11].

Porous adsorbents were shown to be promising for post-combustion carbon capture [12]. For such an alternative a matching research project is presented in this work concerning primarily post-combustion treatment of CO_2. The aim is the discovery and application odds of new, low cost adsorbents and generally energy efficient separation and capture of flue gases. Optimal adsorbents are materials that have high uptake capacity, high separation capacity, stable thermal and mechanical properties, and they allow fast kinetics of adsorbates. Finally, of course, they must be inexpensive, an attribute particularly important for large scale applications. This is the case of the flue gases from the power plants in Western Macedonia where electricity is produced using the subsurface lignite deposits of Florina–Ptolemais–Kozani in the Region of Western Macedonia. Here is actually produced ca the 58% of the total electricity power consumed over the entire Greek state, Fig. 1.



Fig. 1. Map showing the locations of lignite mines in W. Macedonia region in Greece and the zeolite deposits in Evros, North-Eastern border of Greece.

Regarding CO_2 capture and potential storage there are still not yet any data concerning the cost of capture, transport and storage processes. This shortage concerns also transport pipelines, which is considered as a primary means to transport CO_2 from the region of capture to the permanent storage. In spite of that, most cost evaluations of the CO_2 isolation do not include the transport of the gas [9]. Greece appears to have high prospects for CO_2 storage in the "Prinos" depleted offshore oil field.

In the present work the history of energy production and utilization with respect to the economic development in modern Greece will be first reviewed. The background of the low carbon economy generation and development will be revised next. Finally, an intermediate method during the transition period to this drastic socioeconomic and environment friendly change will be presented. It will be based on the CO_2 capture and permanent storage using inexpensive natural resources, aiming isolation of the gas from the active natural processes. The prospective to be investigated is thus the permanent storage of CO_2 in natural geological deposits of zeolites and depleted lignite mines. Natural zeolites are present in altered pyroclastic rocks at many localities in Greece, and large deposits of potential economic interest are present in three areas: (1) the Evros region of the province of Thrace in the northeastern part of the Greek mainland, Fig. 1; (2) the islands of Kimolos and Poliegos in the western Aegean; (3) the island of Samos in the eastern Aegean Sea [13].

Hellenic natural zeolite deposits, Fig. 2, comprises solid crystalline microporous material [15]. The kind, the position as well as the expected amount of this zeolite deposits have to be considered. If they are found to be appropriate they could probably be used to minimize the cost of CO_2 capture and permanent storage.

2. Air pollutants

As air pollutants are characterized any gas substances that can enter either deliberately or through some natural processes in

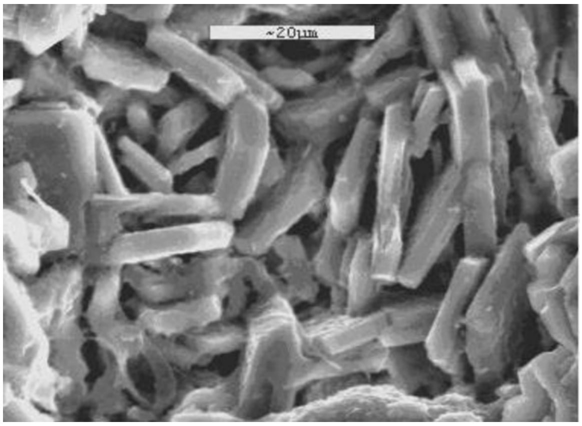


Fig. 2. SEM microphotograph of HEU-type zeolite of Evros, Greece [14].

the atmosphere and which have even an indirect effect on the composition of air. Such are for example oxygen depletion in the atmosphere or any other change of the atmosphere composition through, e.g. increase of primarily, CO, CO_2, or secondarily, O_3, air pollutants.The post-combustion emitted primary gas pollutants are usually oxides; carbon monoxide, CO, dioxide, CO_2, sulfur oxides, SO_2, SO_3, nitrogen oxides, N_2O and NO_x: NO, NO_2. Some of the above gases, mainly CO_2, belong to the GHG (greenhouse gases). Here also belongs methane as well as fluorinated gases [16,17] all the latter created by human activities. They are gases used as refrigerants, driving gases in aluminum packaging and for other industrial purposes. Even though they occur in very low concentrations in the atmosphere, they are still very potent as greenhouse gases contributing 14% to the current warming trend. They include hydro-fluorocarbons (HFCs), chlorofluorocarbons (CFCs), perfluorocarbons (PFCs) and sulfur hexafluoride (SF_6) [18].

Carbon dioxide CO_2 is a natural compound of the atmosphere and it is extremely important for plant metabolism. It is normally found in equilibrium concentration with the other atmospheric gases due to photosynthetic that is the main stabilizer of the O_2/CO_2 ratio in the atmosphere.

The 2011concentration of carbon dioxide in Earth's atmosphere is approximately 392 ppm (parts per million) by volume. The contemporary increasing industrial development and vehicle engine combustion of fossil fuel have led to a concentration rise by 2.0 ppm/year during 2000–2009 [19]. This bias in the balance of carbon dioxide in air composition has been accused for the phenomenon of the greenhouse effect and the global warming.

Our aim in this work is to propose new methods of taming the problem by binding/capturing of at least part of the emitted carbon dioxide by certain human activities [20]. In particular, capturing of carbon dioxide from large point sources allows storage options, such as geological isolation, capable to reduce emission levels in the atmosphere [11].

Carbon capture and storage (CCS) could reduce the amount of carbon dioxide released into the atmosphere [21]. Capture is more costly compared to the storage process, but the overall cost of isolation of anthropogenic CO_2 is too high for a straightforward implementation in the current global energy balance. The potential for more cost-effective technologies for post combustion capture is the subject of further ongoing research.

Another important issue of efficient CO_2 isolation comprises the transportation of the gas to the final storage location with the injection into a storage site. A further issue in the future is also recycling the stored CO_2 for example by catalytic reduction to methanol.

CO_2 has been used by industries for several decades until present time for enhanced oil recovery (EOR) applications and therefore, large-scale transport of CO_2 is not a new technology [22]. Pipelines can be considered as the primary means of transporting CO_2 from the point-of-capture to site where it will be stored permanently. Also use of ship transport for CO_2 has been proposed as an alternative instead for pipeline transport but it is difficult to realize due to non-accessibility by sea of many possible CO_2 sources and sinks [22].

Table 1
Greenhouse gas (GHG) emissions (Mt CO_2 eq) of the EU-27 [23].

GHGs (Mt CO_2 equivalent)	1990	2000	2005	2020	2030
All GHGs	5578	5101	5177	5496	5380
All CO_2	4379	4128	4267	4610	4639
Emission trading system ETS	–	2290	2340	2557	2573
ETS without aviation	–	2156	2193	2339	2319
Aviation	–	134	147	218	255
Non-ETS sectors	–	2811	2871	2940	2806
Energy related non-ETS	–	1838	1927	2054	2065
Non-CO_2 GHGs	1199	973	944	886	741

2.1. EU GHGs emissions

2.1.1. 1990–2005 trend

The total EU-27 greenhouse gas (GHG) emissions according to European Environmental Agency [24] were equal to 5177 Mt CO_2 equivalents in 2005. This represents a slight decrease (−0.7%) compared to 2004 bringing emissions 7.9% below the 1990 level, Table 1.

2.1.2. 2010–2020 projections

By 2010, the total EU-27 greenhouse gas emissions were projected to be 7.5% lower than in 1990. This projection was based on Member States estimates which take into account all existing domestic policies and measures. The decline compared to 1990 is 11% if additional domestic policies and measures are also taken into account. In the long term, and in the absence of any current global post-Kyoto agreement, projected emissions by 2020 for the EU-27 can be compared to the commitment target of a 20% reduction, unilaterally decided by the European Council in March 2007. A first assessment of 2020 projections by the Member States indicates that greenhouse gas emissions in the EU-27 can be expected to rise after 2010 and to be 6% below 1990 levels by 2020, thereby being 2% higher than in 2005. However, these initial 2020 projections do not tend to include the effects from additional policies [24].

2.2. Greek carbon dioxide emissions and commitments

The main reasons for the increase of CO_2 emissions in Greece have the origin in a heavy dependence on lignite for electricity production, the limited renewable energy development and the increase of energy consumption per capita by 50% during the past 10 years. The average increase per capita for the rest of Europe has been 5% for the same period [25].

The Kyoto protocol was adopted in 1997 and was put into force aiming the 2005 set targets of reduction of GHGs emissions for 37 industrialized countries and the EU [26]. Greece developed its action plan for the abatement of CO_2 in February 1997. Greece's GHGs emissions within the 2008–2012 period should not exceed an increase of 25% compared to 1990 levels (historical base year) while the EU target for the same period was to reduce the emissions by 8% [27]. Carbon dioxide emissions account for approximately 79.7% of the total emissions of air pollutants in Greece while methane accounts for 8.1% and nitrous oxide for 8.2%. The other three F-gases contributed the remaining 3.3% [28].

The emission of the GHGs is estimated to further increase by ca 20% in the next 10 years' period until 2020 as seen in Table 2. The development of the GHGs emissions and the corresponding

Table 2
Evolution of total GHGs emissions in Greece (kt CO_2-eq).

	1990	1995	2000	2005	2010	2015	2020
Total GHGs	106,145	110,120	133,789	137,435	147,206	158,046	169,536
CO_2	85,586	87,273	107,817	111,962	120,816	128,947	136,834
GHGs excess %	Base year	3.74%	26.04%	29.47%	38.68%	48.89%	59.72%

emission excess with respect to year 1990 for each new 5-year period is also reported.

Greece's GHG emissions derive mainly from lignite and oil. The actual energy mix for the electricity generation in Greece is composed by 49% of lignite, 9% of oil, 17% of natural gas, 17% of renewable energy sources (RES), and 9% imports. Electricity generation produces about 45% of the CO_2 emissions in Greece, transport for 22.7%, industry 10.9% buildings sector (commercial, public, residential) for 8.9% and refineries for 3.4%. Most CO_2 emissions for the production of electricity come from the use of lignite ca 45%.

As seen in Table 3, Greece's overall CO_2 emissions profile shows a clear domination by the energy sector. In 1990 CO_2 accounted for 80/63% of the total GHGs emissions followed by N_2O and CH_4. A similar pattern was reported in 2000 and 2010 when the proportion of CO_2 was also 80/58% and 82/70%, respectively. The projection for 2020 shows that the ratio GHG/CO_2 will remain invariably 80/71%.

On the emission of carbon dioxide in particular is focusing Table 3. It contains also the distribution of the emissions on the main national sectors of interest. One should notice the overwhelming partition of the CO_2 emissions from the energy production, which is furthermore approximately one order of magnitude greater than the industrial consumption irrespective any during given time period.

There is a long standing debate in the world on the need to introduce new policy instruments for the CO_2 abatement. Oil, coal and natural gas will remain the world's dominant sources of energy over the next decades, with resulting carbon dioxide emissions set to increase to unsustainable levels. However, technologies that help reduce CO_2 emissions from fossil fuels reverse this trend. CCS technology is particularly promising, because it takes CO_2 from large stationary sources and stores it to prevent its release into the atmosphere [21].

The EU set a series of demanding climate and energy targets to be met by 2020, known as the "20-20-20" targets. These are: (a) a reduction in EU greenhouse gas emissions of at least 20% below 1990 levels; (b) 20% of EU energy consumption to come from renewable resources; (c) a 20% reduction in primary energy use compared with projected levels, to be achieved by improving energy efficiency. As seen in Table 4, the Greek plan known as "20-20-20" on climate and energy targets set by the EU describes a major increase in the share of renewable energy sources in the country's energy mix. Yet the role of lignite appears to remain important even in the long-term for Greece's electrical energy production.

In the face of that, a plan is needed to tackle the adverse economic and environmental effects of lignite power production in Greece. The plan sets a binding national goal of achieving a 20% share by renewable energy sources (RES) in power production (40% share in electricity production) by 2020, which is more than the 18% goal originally set by the EU's renewable energy directive for Greece. 10% of fuel used in transportation is projected to derive from bio-fuels by 2020. Major investments in renewables are intended to achieve the goal of 4% reduction of greenhouse gas production by 2020, compared to 2005 [30].

3. Progress with carbon capture and storage, CCS

Fossil fuel contributes to 81% of the world's commercial energy supply and therefore combustion of fossil fuel triggers severe global warming. In order to stabilize the level of CO_2 in the atmosphere CCS should be rapidly introduced [31]. There are methods based in physicochemical techniques, such as cryogenic separation (distillation) and separation of CO_2 gas using solvents, which is also the most common technique [10]. However, the cost of these known ordinary methods for carbon capture is very high and it is urgent to reduce this cost significantly. More advanced current post-combustion adsorption-driven carbon capture and separation methods of carbon dioxide with porous materials are the membrane-based separations and the separation with sorbents pressure/vacuum swing adsorption (PSA/VPSA) as well as temperature swing adsorption (TSA). These adsorption-driven carbon capture methods and the electrical swing adsorption (ESA) have attracted much attention because of their low energy cost and environmental friendly characteristics [31].

3.1. Methods of gas separation

There are several mechanisms for membrane separation: Knudson diffusion, molecular sieving, solution-diffusion separation, surface diffusion including adsorption and capillary condensation. Three of these are schematically represented in Fig. 3. Molecular sieving and solution diffusion are the main commonly used mechanisms for nearly all gas separating membranes [11].

Knudsen separation is based on gas molecules passing through membrane pores small enough to prevent bulk diffusion. Separation is based on the difference in the mean path of the gas molecules due to collisions with the pore walls, which is related to the molecular weight, Table 5. The relative selectivity for any gas pair is determined by the inverse ratio of the square root of their molecular weight. For CO_2/N_2 and CO_2/H_2 separation in particular, Knudsen diffusion predicts a selectivity of less than unity, i.e. 0.987 and 0.213, respectively. Consideration of the above data indicates that this method is not appropriate for the purpose of CO_2 separation in flue gases. On the other hand the following molecular sieving separation mechanism can be applicable for the purpose of the present work.

Table 3
Evolution of CO_2 emissions in Greece (1990–2020) (kt CO_2-eq), Ref. [29].

Year/sector	1990	1995	2000	2005	2010	2015	2020
Energy	76,474	79,778	95,682	102,083	110,838	118,866	126,647
Industry	7686	7709	7877	7929	8026	8126	8230
Solvents	177	156	169	173	177	179	181
Forests	1249	−370	4090	1776	1776	1776	1776
Total	85,586	87,273	107,817	111,962	120,816	128,947	136,834

Table 4
Greece's energy mix targets "20-20-20" in MW.

Electrical power	2010	%	2015	%	2020	%	2025	%	2030	%
Lignite	4826	32.59	3992	19.50	3362	12.50	2295	7.88	2295	7.16
Petrol. products	2109	14.24	1344	6.56	1345	5.00	1349	4.63	1334	4.16
Natural gas	3349	22.62	5810	28.38	7211	26.82	8324	28.58	9170	28.60
Biomass/Biogas	60	0.41	120	0.59	250	0.93	370	1.27	500	1.56
Hydroelectric	3237	21.86	3615	17.66	4531	16.85	4531	15.56	4531	14.13
Wind Energy	1042	7.04	4303	21.02	7500	27.90	8750	30.04	10,000	31.19
Photovoltaics	184	1.24	1270	6.20	2567	9.55	3167	10.87	3833	11.95
Geothermal	0	0.00	20	0.10	120	0.45	340	1.17	400	1.25
Total (MW)	14,807	100	20,474	100	26,886	100	29,126	100	32,063	100

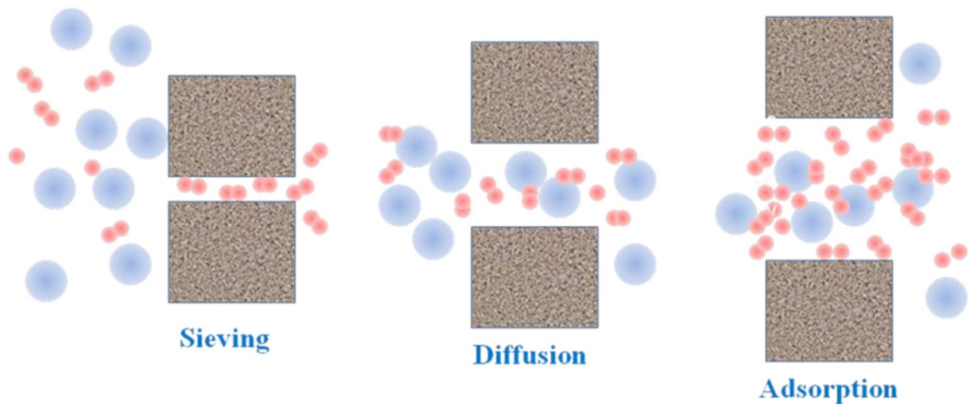


Fig. 3. Schematic representation of three different possible mechanisms for membrane gas separation, molecular sieving (size exclusion), Knudsen diffusion, and adsorption (physi- and chemi-sorption).

Table 5
Molecular gas-kinetic diameters from Ref. [11]. The last row is determined by viscosity measurements from Malkov et al. [32] and Deshman [33].

Gas	CH_4	NH_3	H_2O	N_2	CO	O_2	CO_2	Air
MW	16	17	18	28	28	32	44	–
Diameter	3.8	–	2.65	3.64	–	3.46	3.3	–
(Å)	4.19	2.97	–	3.70	3.70	3.64	4.65	3.74

In particular, the separation of gas mixtures by molecular sieving relies on size exclusion. The sizes of the active membrane pores are carefully controlled relative to the kinetic (sieving) diameter of the gas molecule. This allows a much faster diffusion rate of smaller gas molecules vs. larger ones. In this case, the CO_2/N_2, selectivity is greater than unity, as CO_2 has a smaller kinetic diameter than N_2 [11].

A closer look in Table 1 indicates that methods based on viscosity are not appropriate for the purpose of the present work.

3.2. Adsorption in coals

In the case of gas adsorption in coals, the microporous coals diffusion is activated and the apparent micropore diffusivities of gases in coal decrease strongly with increase in gas kinetic diameters [16]. A selective adsorption and transport study concerning CO_2, N_2, CH_4 gases in coal particles were recently undertaken [16]. Activated carbon can be manufactured from carbonaceous material, including coal (bituminous, subbituminous, and particularly lignite[1]), peat, wood, or nutshells, e.g. coconut. The manufacturing process consists of two phases, carbonization and activation but it is complicated and costly. The coal matrix is heterogeneous, containing firstly macropores of both non-constricted and highly constricted type, which only allow CO_2 to permeate [34]. The same material contains also ultra micropores that only adsorb CO_2 due to carbon dioxide smaller kinetic diameter. Furthermore the CO_2 is also competitively adsorbed by larger pores because of its larger affinity [16]. The apparent micropore diffusivity of CO_2 is generally one or two order of magnitude higher than those of CH_4 and N_2 because of their kinetic diameters relation $CO_2:N_2:CH_4 = 0.33:0.36:0.38$ nm. Hence, there is a strong selective diffusion of CO_2 over CH_4.

Furthermore, in contrast to all available theoretical data,[2] the apparent macropore diffusivity of CO_2 is also larger than those of CH_4 and N_2, suggesting that coal has an interconnected but highly constricted pore network by ultra micropores with width 0.6 nm [16].

In the same work was shown that the apparent diffusivity strongly decreases with an increase in gas pressure, attributed to coal matrix swelling caused by gas adsorption. Swelling leads in turn to micropore entrance narrowing that increases the diffusion energy barrier of adsorbate in micropores. The strong variation of the diffusivity with increase in pressure indicates strong effects on gas transport in coal seams (layers).

[1] The question is if we also can use depleted lignite mines for permanent CO_2 storage. The potential saving is enormous since the combustion stations are in the realm of the mines.

[2] The kinetic diameter data determined by viscosity measurements portray CO_2 molecular diameters greater than N_2, Table 5.

3.3. Experimental study and modeling of CO_2 adsorption and separation

Many research groups worldwide focus in separation, capture and long term storage of CO_2 gas [12]. These attempts involve developing and testing new methods and materials for separation of CO_2 from combustion gas admixtures. The composition of combustion exhaust of power plants-flue gas-depends on the material burned. It typically consists of more than two-thirds (2/3) nitrogen and excess oxygen derived from the combustion air, as well as carbon dioxide and water vapor. It contains also a small percentage of pollutants such as solid matter in the form airborne particles, carbon monoxide, nitrogen oxides and sulfur oxides. A simulated flue gas considering usual composition of 13.55% CO_2, 3.86% O_2, 72.72% N_2 and 9.87% H_2O was used in [35].

Advanced methods of modeling gas adsorption were tested aiming to invent and develop methods enhancing selectivity, adsorptivity, durability and transport properties of porous materials [31,35]. The project seeks competence in several stages of the CO_2 isolation task through, e.g. multiscale modeling from the molecular level to macroscopic conditions. It involved model building and molecular dynamics simulations, as well as Grand Canonical Monte-Carlo (GCMC) simulations. One important part concerned modeling of gas separation and capture by selective adsorption in porous materials. Adsorption and transport inside porous materials of CO_2 and nitrogen were particularly studied [36,37]. The results so far show that both physic- and chemic-sorption are operative.

Characterization studies of CO_2 uptake and selectivity were performed while tests were performed aiming organic surface modification, innovative powder processing and synthesis of new porous adsorbents. Several results were obtained such as for example that water enhances the uptake of CO_2 and also that some organic materials important for the method improvement. The ultimate goal was to discover the optimal adsorbent substances for these processes. Some novel porous materials were investigated, such as, new zeolite related microporous materials, chiral mesoporous materials, carbon mesoporous materials, metal-organic and covalent-organic framework materials, and porous materials using bimolecular templates [38].

A comprehensive review concerning nanoscale sorbent materials that have been developed and the theoretical basis for their function in CO_2 separation, particularly from N_2-rich flue gases, is published recently [12].

3.4. Silica functionalized with propylamine groups

Amine-modified silica adsorbed significant amounts of CO_2, especially at the low partial pressure, which is important for CO_2 capture from flue gas. One of the systems studied was on alkylamino-modified amorphous silica surfaces. Mesoporous silica particles (Davisil) were functionalized with amino-propyl-tri-ethoxy-silane (APTES) in a fractional factorial design with 19 different synthesis and uptake experiments. Most important to functionalization was the amount of water present during synthesis, the reaction time, and pretreating the silica with a mineral acid [38].

Modeling and simulation of adsorption of CO_2 on this substrate was performed using Grand Canonical Monte Carlo (GCMC) simulations. The first aim was to locate the global minimum sites for CO_2, revealing a wealth of 15 such global minima. A closer look at these minima allowed by this method showed that they were actually due to typical hydrogen bonds formed between —NH_2 and CO_2.

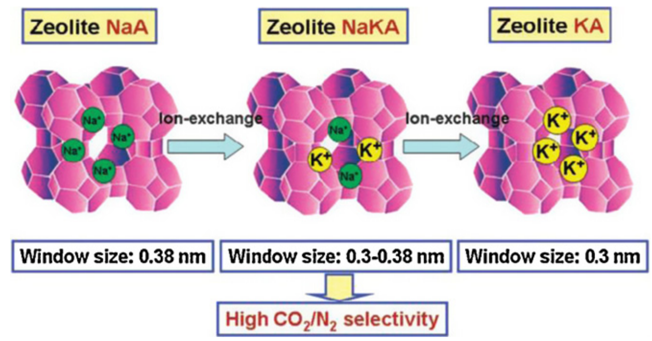


Fig. 4. Illustration of the reduction of the effective pore window aperture in NaKA zeolite by Na^+ exchange by K^+ as a mechanism improving the zeolite CO_2/N_2 selectivity.
Adopted from Ref. [31].

3.5. Adsorption of CO_2 in zeolites

Among the known applications of zeolites are drying of process air, CO_2 removal from natural gas, CO removal from reforming gas, air separation, catalytic cracking, and catalytic synthesis and reforming. Zeolites can be used to separate CO_2 from gas mixtures but the adsorption selectivity is genetically low. However, an experimental and theoretical work on the CO_2/N_2 separation by NaKA zeolite performed by Hedin, Laaksonen et al. [31] showed that it is possible to improve this property. The uptake of carbon dioxide and nitrogen gas by zeolite NaKA was studied in that work.

Illustration of the structural mechanism by which Na^+ ion exchanged by the larger K^+ reduces the effective pore window aperture in NaKA zeolite is seen in Fig. 4. The 8-ring zeolite A has pore size 0.38 nm, which is comparable to the size of the kinetic diameters of the CO_2 and N_2 gas molecules, 0.33 nm and 0.364 nm, respectively (see footnote 2). By ion exchange of the Na^+ ion by K^+ the pore-size was possible to tune so that the selectivity of the zeolite in CO_2 was increased. A very high ideal CO_2-over-N_2 selectivity and a high CO_2 adsorption capacity were observed at an optimal K^+ content of 17 atoms% rendering NaKA, Fig. 5, a very promising adsorbent for CO_2 separation from water-free flue gases generated during post combustion processes [31].

The experimental results obtained in that work by SEM, adsorption data, XRD patterns and FTIR spectra, were compared with computational modeling. In particular GCMC (Grand Canonical Monte Carlo) simulations of adsorption of CO_2 and N_2 inside Zeolite A with varied Na^+/K^+ composition were constructed, algorithms

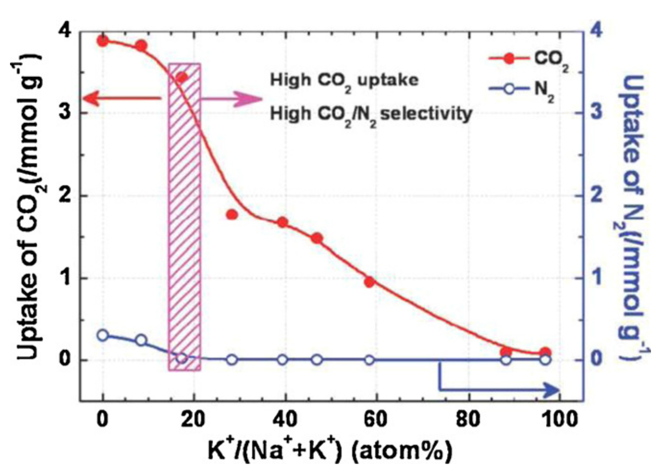


Fig. 5. Experimental CO_2 and N_2 uptake vs. Na^+/K^+ ion ratio (298.15 K, 0.85 bar) in NaKA adopted from Ref. [31]. Lines are provided to guide the eye.

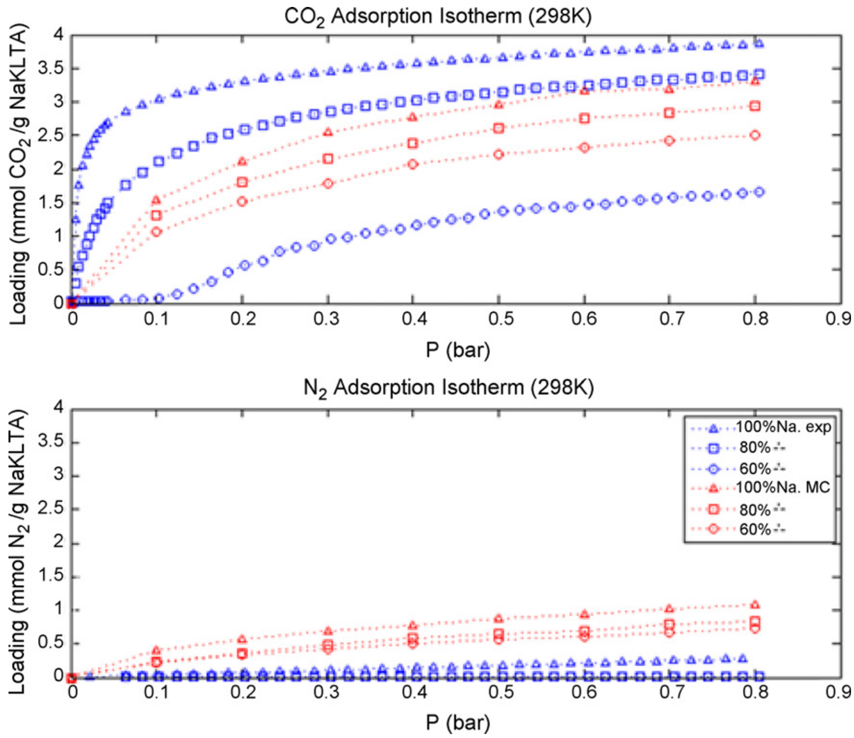


Fig. 6. Theoretical (red) and experimental (blue) adsorption isotherms (gas loading vs. pressure) of CO_2 gas (higher panel) and N_2 (lower panel) inside Zeolite A with varied Na^+/K^+ composition [39]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

that are commonly utilized in simulations of gas adsorption in zeolites [31]. The positions of the cations in the NaKA zeolite were localized using an energy minimization procedure (MC simulated annealing in the canonical ensemble). The adsorption isotherms for the CO_2 and N_2 gases were then obtained in the grand canonical ensemble at 298.15 K for a series of fixed pressures, and these isotherms were compared with the experimental data, Fig. 6.

The calculated levels MC simulations of N_2 uptake were consistently higher than the experimentally measured uptake levels (Fig. 6) showing that the thermodynamic effects are not sufficient to describe the CO_2/N_2 separation of the system. Therefore, while the trends were reproduced, the MC simulations did not quantitatively reproduce the experimentally observed high CO_2-over-N_2 selectivity. As seen in Fig. 6 the uptake increases with Na content for both gases and the overall adsorption of CO_2 is always greater. Some additional conclusions were also obtained. Both the uptake of CO_2 and the CO_2/N_2 selectivity are decreasing with the temperature increase [36].

It is worth to mention another important property of the zeolite NaKA adsorbent, the ability to recycle. The regenerability of the NaKA zeolite by conducting cycle measurements [31,36]. It was shown that the regeneration temperature was important for zeolite regeneration. When the regeneration temperature decreased to 473 K, the uptake of zeolite NaKA decreased dramatically. After increasing the temperature back to 623 K again, the uptake of the sample returns to the high value. Furthermore these investigators remarked that the decrease of the uptake after the first cycle was caused by the chemisorption of CO_2 on the zeolite [2].

4. The prospective of using Greek zeolite deposits

Natural zeolites form in several geological environments such as hydrothermal, burial metamorphic, closed system (including alkaline lakes), open system and weathering profiles [40]. More than 50 distinct species of natural zeolites and 100 types of synthetic zeolites are known at present.

In the province of Thrace, northeastern Greece exist zeolite deposits of both sedimentary and hydrothermal origin that are rich in heulandite and/or clinoptilolite. The deposits at the location metaxades (Fig. 7) can be classified as heulandite although this deposit was first described as clinoptilolite [13]. The distinction between heulandite and clinoptilolite, which belongs to the heulandite family, should be made on the basis of Si/A1 ratio (>4 for clinoptilolite, <4 for heulandite). According to Refs. [41,42], the basis in dividing the group is the predominant exchangeable cation, i.e. in heulandite Ca > (Na + K) and in clinoptilolite (Na + K) > Ca. Electron microprobe analyses of the metaxades deposit show that Ca is the principal cation, i.e. Ca > (Na + K) and also that K >> Na, although the Si/A1 ratio is greater than 4 [43]. The metaxades zeolite deposit also breaks down on heating ~500 °C, which is typical of heulandite but not clinoptilolite. Nevertheless it was found that minor amounts of K-rich clinoptilolite and mordenite coexist with the predominant heulandite in the metaxades deposit [43].

The confirmed subsurface deposit is ca 70 Mton and the deeper 500 Mton. The Greek natural zeolite reserves contains 89 wt.% Heulandite HEU-type zeolite, 3 wt.% mica + clay minerals, 5 wt.% feldspars and 3 wt.% quartz. The chemical formula of the, HEU-type zeolite is: $Ca_{1.5}K_{1.4}Mg_{0.6}Na_{0.5}Al_{6.2}Si_{29.8}O_{72}\cdot 20H_2O$ and the ammonium exchange capacity is 226 mequiv./100 g. The chemical composition is 68.62 wt.% SiO_2, 11.80 wt.% Al_2O_3, 2.92 wt.% K_2O, 2.14 wt.% CaO, 1.13 wt.% Na_2O and 0.75 wt.% MgO [14].

Clinoptilolite-K	$|(K,Na,Ca_{0.5},Sr_{0.5},Ba_{0.5},Mg_{0.5})_6(H_2O)_{20}|[Al_6Si_{30}O_{72}]$
Clinoptilolite-Na	$|(Na,K,Ca_{0.5},Sr_{0.5},Ba_{0.5},Mg_{0.5})_6(H_2O)_{20}|[Al_6Si_{30}O_{72}]$
Clinoptilolite-Ca	$|(Ca_{0.5},Na,K, Sr_{0.5},Ba_{0.5},Mg_{0.5})_6(H_2O)_{20}|[Al_6Si_{30}O_{72}]$

Some high quality HEU-type natural zeolites, Fig. 8, display unique physical and chemical features and have a great variety of environmental, industrial and agricultural applications. The large natural zeolite deposits and the low cost of mining, gave access to large-scale utilization [42,44].



Fig. 7. Natural zeolite deposits in metaxades Greece and church constructed from zeolite taken from the particular deposit.

Zeolite A is a synthetic sodium aluminium silicate with the formula $Na_{12}(AlO_2)_{12}(SiO_2)_{12}\cdot 27H_2O$. The cubic microcrystals have an optimized particle shape (rounded corners and edges) and an average particle diameter of 3.5 μm. Zeolite A has purity greater than 99%. Trace impurities may consist of Fe_2O_3 (<0.2%) and amorphous alumosilicates.

Zeolite A exhibits the LTA (Linde Type A) structure. It has a three-dimensional pore structure with pores running perpendicular to each other in the *x*, *y*, and *z* planes, and is made of secondary building units 4, 6, 8, and 4-4. The pore diameter is defined by an eight member oxygen ring and is 4.2 Å. This leads into a larger cavity of minimum free diameter 11.4 Å. The cavity is surrounded by eight sodalite cages (truncated octahedra) connected by their square faces in a cubic structure. The unit cell is cubic (a = 24.61 Å) with $Fm{-}3c$ symmetry. Zeolite A has a void volume fraction of 0.47, see Fig. 9, with a Si/Al ratio of 1.0. It thermally decomposes at 700 °C [45].

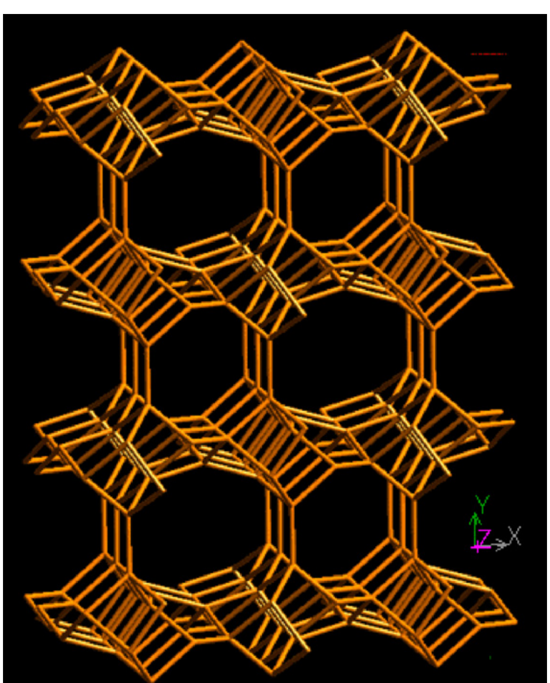


Fig. 8. The structure of HEU type zeolite.

4.1. Adsorption capacity of zeolites

Referring to the recent work [31], the optimal experimental CO_2-over-N_2 uptake of the NaKA zeolite is according the diagram in Fig. 5 ca 3.2 mmol/g = 3.2 mol/kg zeolite, occurring for relative K^+ ionic ratio of 17% or ionic K^+/Na^+ ratio 17/83. The conditions of the experimental conditions of the adsorption were rather mild, ca 25 °C and 0.85 bar = 0.839 atm. The above optimal K^+ content of the ion exchanged NaKA yields a high ideal CO_2-over-N_2 selectivity of 172 times, and this value is much higher than that in zeolite NaA, X, Y, ZSM-5 and beta zeolite. The capacity of NaKA zeolite to adsorb CO_2 was similar to the capacity of NaA zeolite, 3.88 mmol/g.

The adsorption capacity of the NaKA zeolite can be transformed to more practical equivalent CO_2 adsorption capacities, i.e. 140.8 kg CO_2/ton NaKA. This would also correspond to a volume CO_2 under normal P/T conditions equal to 71.68 m^3/ton NaKA. The same experimental data show that the uptake of the mainly coexisting in the flue gases N_2 by the zeolite would be comparably insignificant due to the differential selectivity of the optimally ion exchanged NaKA zeolite [31].

The facts so far do not discourage the possibility of using natural deposits of zeolites similar to NaKA as an inexpensive way for permanent storage of CO_2, if some other conditions are also equally convincing. Except for the transport and the actual process of adsorption, another important aspect in the context of long term storing the CO_2 adsorbed in the natural surface zeolite deposits are the conditions of retained adsorptivity.

Further experimental evidence on the NaKA zeolite showed that it was more difficult to remove CO_2 at higher K^+ contents. However, at 17 at.% of K^+ in NaKA, most physisorbed CO_2 could be removed only after applying dynamic vacuum conditions, leaving very little CO_2 remained in the zeolite. This fact indicates that under natural conditions the CO_2 can safely stored under very long periods.

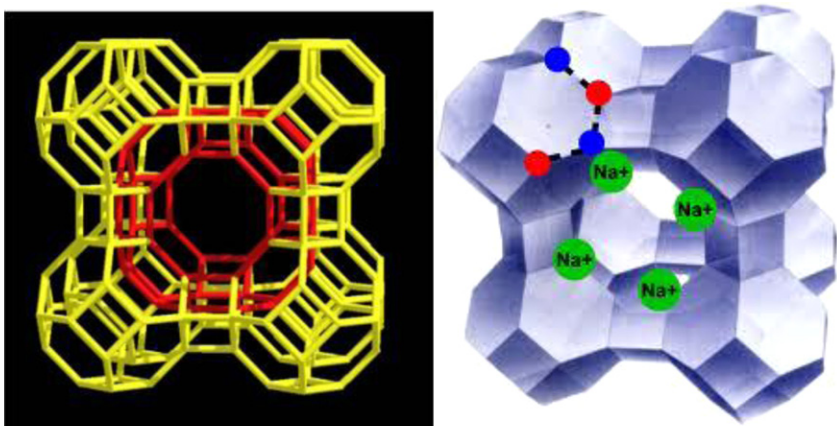


Fig. 9. (Left) Zeolite A structure type LTA [13]. (Right) Clinoptilolite.

5. Discussion

Except for zeolites an interesting alternative in the case of the energy productions in Greece from lignite will be discussed here. In addition, a discussion of the problem of the CO_2 transport from the area of energy production to the area of permanent deposition is undertaken.

Carbon capture and storage (CCS) is considered as one of the most promising technological options for the mitigation of CO_2 emissions from the power generation sector and other carbon-intensive industries that can bridge the transition period between the current fossil fuel-based economy and the renewable and sustainable technology era [6,46].

CCS involves capture of CO_2 from the sources, transport of CO_2 through dedicated pipelines and ships, and the storage of CO_2 in geological reservoirs, such as depleted oil and gas fields and saline aquifers, for its permanent isolation from the atmosphere [47].

The development of CCS technologies has increased significantly in the last decades; however, there are still major gaps in knowledge of the cost of capture, transport and storage processes. Pipelines have been identified as the primary means of transporting CO_2 from point-of-capture to site where it will be stored permanently but there is little published work on the economics of CO_2 pipeline transport and most cost studies either exclude transport costs or assume a given cost per ton of CO_2 in addition to capture costs. Certain technical and economic characteristics of a CO_2 transmission pipeline infrastructure are included in a EU commission report [48]. The aim of that report was to identify the elements that comprise a CO_2 pipeline network, provide an overview of equipment selection and design specific to the processes undertaken for the CO_2 transport and to identify the costs of designing and constructing a CO_2 transmission pipeline infrastructure [48].

It is well known that selective adsorption and transport of gases in coal particles of depleted coal seams are important for natural gas recovery. The same properties can be used for carbon sequestration for environmental remediation from CO_2 stored in adsorbed state as studied in [16]. A question that we will pose in this work is if part of the lignite deposits, obviously the most energy poor, are appropriate for long term CO_2 storage. Since the deposits of lignite are in the region of Ptolemais in Western Macedonia, Greece, where the energy production occurs there will be an extremely economical solution.

In [16] the interaction energies of adsorbates and micropores with various widths were investigated using a slit-shape pore model. Experimental adsorption rate data of the three gases, CO_2, CH_4, and N_2, were conducted on the same coal sample and were compared to numerical simulations using a bidisperse model rendering the apparent diffusivities of each adsorbate in the macropore and micropore samples. The results indicated that the relative adsorbate molecule size and the pore structure play an important role in the selective gas adsorption and diffusion in micropores. In both microporous and macroporous coal, CO_2 showed greater experimental diffusivity compared to CH_4, and N_2. The significantly higher diffusivity of CO_2 in microporous coal was verified theoretically while theory was unsuccessful in macroporous [16].

6. Conclusions

It is of great socioeconomical and environmental value to perform an extensive investigation for the possibility of a large scale capture and permanent storage of CO_2 through burial in the Greek depositions of clinoptilolite and/or low coal content lignite. Except for the physicochemical research questions to be answered such a project can contribute to the local developments of poor and polluted regions of Greece and decisively enhance the development of a global, intermediate, sustainable method of low carbon economy. We can preliminarily give an order of magnitude of a total amount of CO_2 that can be permanently buried in the known deposits of Zeolite in northern Greece [49]. Considering an easily available surface and subsurface amount of zeolite of 570 Mton and using the data of Section 4.1, adsorption capacity 140.8 kg CO_2/ton NaKA zeolite, it is estimated that the total capacity of only these deposits would be 79.8 Mton CO_2.

Appendix A. Survey of additional references in the network

Selected here are presented WEB pages pertinent to the subject of GHG and atmospheric pollutants among the enormous amount of similar Internet appearances.

1) http://data.worldbank.org/indicator/EN.ATM.METH.KT.CE (methane emissions, kt of CO_2 equivalent)
2) http://www.acoolerclimate.com/fluorinated-gases/ (fluorinated gases)
3) http://en.wikipedia.org/wiki/Flue_gas (flue gas)
4) http://izasc.ethz.ch/fmi/xsl/IZA-SC/ftc_fw.xsl?-db=Atlas_main&-lay=fw&-max=25&STC=HEU&-find (framework type HEU)
5) http://www.zeolife.co.uk/what%20is%20natural%20zeolite.htm (clinoptiloline channel structure)
6) http://ec.europa.eu/clima/policies/f-gas/docs/report_en.pdf (European Commission: Report on fluorinated GHG

7) http://www.epa.gov/climatechange/emissions/downloads10/Subpart-L_RTC.pdf (mandatory GHG reporting rules by the US Environmental Protection Agency)
8) http://en.wikipedia.org/wiki/Kyoto_Protocol (Kyoto protocol)
9) http://en.wikipedia.org/wiki/Carbon_dioxide_in_Earth%27s_atmosphere (atmospheric balance of CO_2)
10) http://en.wikipedia.org/wiki/Adsorption (physics of adsorption)
11) http://www.heraproject.com/ (Human & Environmental Risk Assessment, HERA 2004. risk assessment of sodium aluminium silicate)

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